ORIGINAL ARTICLE

Enhancing ceria slurry performance for shallow trench isolation chemical mechanical polishing through non-ionic surfactant addition

Lifei Zhang[1] · **Lile Xie**[1] · **Xinchun Lu**[1]

Abstract

Chemical mechanical polishing (CMP) is a committed step in the manufacturing of integrated circuits, especially in the fabrication process of shallow trench isolation (STI) structures. Ceria (CeO_2) slurry is widely used in the STI CMP process, while it is vulnerable to causing surface defects owing to particle agglomeration, such as scratches and abrasive residues. Furthermore, CeO_2 slurry faces the challenge of low polishing removal selectivity between silicon dioxide (SiO_2) and silicon nitride (Si_3N_4) surfaces. In this study, we investigated the effects of various non-ionic surfactants and different pH levels in CeO_2-based slurries on material removal rates, removal selectivity, and surface qualities of polished wafers. Two of the studied non-ionic surfactants that make CeO_2 slurries disperse better were selected through sedimentation experiments, which were polyethylpyrrolidone (PVP-K30) and polyethylene glycol, respectively. Subsequently, polishing experiments and atomic force microscopy characterization tests were conducted to illustrate the effects of the selected surfactants at different pH conditions. To further explore the underlying mechanism, the reaction of surfactants on SiO_2 and Si_3N_4 wafers was explained using surface adsorption tests, thermogravimetry experiments, zeta potential measurements, and chemical valence bond structure analysis. As a result, it can be concluded that the performance of ceria slurries used in STI CMP process can be improved by the addition of non-ionic surfactant PVP-K30.

Keywords Shallow trench isolation · Chemical mechanical polishing · Ceria slurry · Non-ionic surfactants · Polyethylpyrrolidone

1 Introduction

Shallow trench isolation (STI), the most frequently used device isolation technology today, is an approach to achieve isolation by etching the silicon substrate who has a topped layer of silicon nitride (Si_3N_4), to form an isolation trench and fill it with insulating dielectric such as silicon dioxide (SiO_2) [1]. Chemical mechanical polishing (CMP) is considered as the indispensable planarization technique in integrated circuit manufacturing and a key step in the fabrication of STI structures [2]. In the CMP process of STI, compared with the traditional silica slurries, ceria (CeO_2) slurries have a higher material removal rate on SiO_2 and greater removal selectivity between SiO_2 and Si_3N_4, while it is still insufficient to meet the strict specification that the removal selection ratio between SiO_2 and Si_3N_4 is supposed to be greater than 20:1 [3–5]. Therefore, the preparation and modification of ceria slurries have been becoming a popular research topic.

The material removal rate (MRR) of Si_3N_4 can be controlled by introducing appropriate surfactants into CeO_2-based slurries, thus achieving high selectivity [6]. Generally, compared with ionic surfactants, non-ionic surfactants have two distinct advantages: first, non-ionic surfactants have an ability to maintain or even improve the removal selectivity between SiO_2 and Si_3N_4 while inhibiting the removal of Si_3N_4; second, the use of non-ionic surfactants can enhance the stability of CeO_2 slurries and thus improve the surface qualities of polished SiO_2 and Si_3N_4. Cho

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et al. [7] demonstrated that the introduction of the surfactant polyacrylic acid in CeO_2-based slurries can strongly reduce Si_3N_4 MRRs, through adsorbing only on Si_3N_4 surfaces and thus forming a dense passivation layer to control the removal selectivity between SiO_2 and Si_3N_4. Veera et al. [8] showed that at pH values of 4 and 5, cyclic amine surfactants, namely pyridine HCl, piperazine, and imidazole, could effectively decrease Si_3N_4 MRRs without affecting the removal rates of SiO_2. Praveen et al. [9] added surfactants l-glutamic acid and l-proline into a synthesized CeO_2-based slurries, both of which could achieve high selectivity between SiO_2 and Si_3N_4. However, the current research on non-ionic surfactants has several deficiencies that the qualities of polished SiO_2 and Si_3N_4 surfaces which directly affect the following fabricating process are inadequate, including the number and depth of scratches, as well as surface roughness. Moreover, the explanation of the action mechanism mainly focuses on the adsorption of SiO_2 and Si_3N_4 wafer surfaces, but ignores the effect of surfactants on zeta potentials of CeO_2 particles and other aspects. On the other hand, pH levels also play a crucial role in removal rates and corresponding selectivity between SiO_2 and Si_3N_4 surfaces [10–12]. Manivannan et al. [10] found that a CeO_2 based slurry with DL-aspartic acid could present high removal selectivity between SiO_2 and Si_3N_4 only in the pH ranges of 4 to 5, where at low pH values, the removal rates of SiO_2 and Si_3N_4 were slow, whereas at high pH conditions, the removal rates of SiO_2 and Si_3N_4 were not significantly inhibited. Suphantharida et al. [11] found that with the increase of pH, silicate adsorption first increases and then decreases, reaching a maximum at about pH 9, and this adsorption may directly participate in the removal mechanism of SiO_2 and Si_3N_4 in the CMP process. Kim et al. [12] demonstrated that pH values affect the colloidal interactions between anionic polyelectrolyte additives and SiO_2/Si_3N_4 surfaces, with the maximum selectivity obtained for SiO_2 and Si_3N_4 at pH 7.

In order to enhance the stability of CeO_2 polishing slurry and improve the surface quality of polished SiO_2/Si_3N_4,

non-ionic surfactants were introduced into CeO_2-based polishing slurry. By studying the effect of non-ionic surfactants on the zeta potential of CeO_2 particles, the mechanism of action is explained in more detail and objectively. In addition, the effect of pH value on the removal selectivity of SiO_2 and Si_3N_4 provides a reference for subsequent research on polishing liquid systems.

Here, attention is given to researching the STI CMP process by introducing various non-ionic surfactants into CeO_2-based slurries, aiming to control MRRs, removal selectivity, and surface qualities after CMP process. Five types of non-ionic surfactants were compared, and the two superior surfactants for better dispersion of CeO_2 slurries were selected. The impact of chosen surfactants on MRRs, removal selectivity between SiO_2 and Si_3N_4, and surface characteristics was next investigated by polishing trials at different pH levels. Depth of scratches on polished wafers and corresponding surface roughness, as well as morphology of CeO_2 abrasive particles, were characterized utilizing atomic force microscope (AFM) and scanning electron microscope (SEM), respectively. Moreover, the action mechanisms of surfactants on SiO_2 and Si_3N_4 wafers were investigated thoroughly by surface adsorption tests, thermogravimetric analysis, zeta potential measurements, and chemical valence bond structure analysis, respectively.

2 Experimental

In Fig. 1a, the studied CeO_2 slurries were prepared by ball milling CeO_2 bonded abrasive mixed with five different non-ionic surfactants for 12 h according to the specific mass proportion:zirconia grinding ball with 1 mm diameter:CeO_2 bonded abrasive: each kind of non-ionic surfactant: deionized water (DIW) = 5:1:1:32. When the ratio of the rotational speed of the ball milling tank to the sun disk is 2 (Fig. 1b), the grinding balls are in close contact with the grinding particles, resulting in a better grinding effect on the particles. Then

Fig. 1 a Schematic diagram of ball milling method. b Changes in abrasive particles before and after ball milling
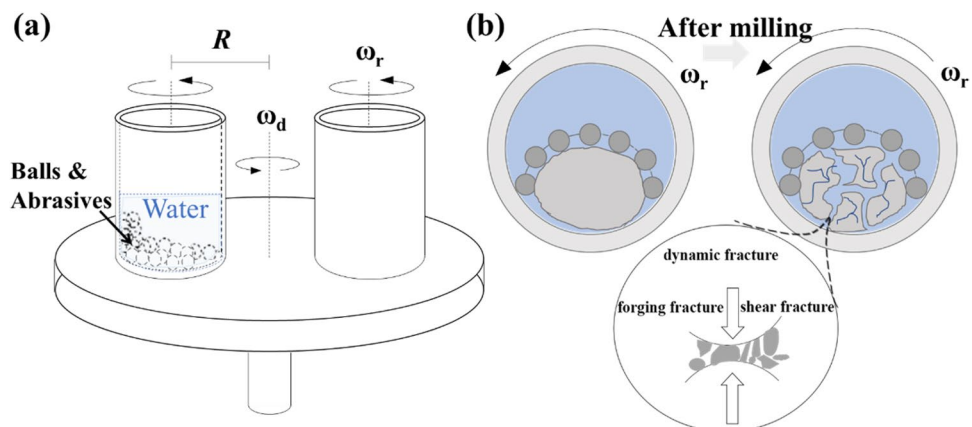
sedimentation experiments were performed for 0 and 7 days to evaluate the delamination outcomes in order to select the efficient surfactants with the best dispersibility and stability. The employed slurries for all CMP tests and other measurements were made by diluting the selected suspension by 100 times.

Polishing experiments were conducted on a Universal 150 Plus Polisher (Hwasting Technology) with a type of rigid polishing pad (DH3002-T80D30-S20M3S1). All wafers were polished at a slurry flow rate of 150 mL/min with platen/carrier speed of 93/87 rpm for 60 s. Prior to each experiment, pad break-in conditioning was conducted for 600 s using a diamond disk. After polishing, all wafers were rinsed with DIW and dried with nitrogen gas in sequence. The thicknesses of the polished 4-in SiO_2 and Si_3N_4 wafers were measured using an optical interferometer (F50, Filmetrics) at 81 different locations on each wafer surface followed by averaging. Each experiment was repeated at least thrice, and the obtained data were used to calculate the average material removal rates and standard deviations.

The morphology of modified CeO_2 abrasive particles by non-ionic surfactants was carried out by scanning electron microscope (SU8220, Hitachi) at a voltage of 5 kV. Zeta potentials and particle sizes of the modified slurries were measured using a laser particle size analyzer (Nano-ZS90, Malvern Instrument), where the transparent samples were prepared by diluting (3.125 wt.%) and sonicating of the selected suspension for 300 s (KUDOS) and then vibrating at a speed of 1600 r/min for 300 s in a thermal vortex mixer. For the zeta potential measurement of wafer surfaces, a solid surface zeta analyzer (SurPASS™ 3, Anton Paar) was used. Moreover, thermogravimetric analysis (TGA) of the prepared CeO_2 slurries were performed using a platinum crucible with nitrogen at 0 ~ 750 ℃. A rotating rheometer (Aaton Paar Physica MCR302) was employed to test the rheological properties of the modified CeO_2 slurries. Quartz crystal microbalance (Q-sense, Sweden Biolin Scientific) was used to characterize and analyze the adsorption properties of solid–liquid interface adsorption between the modified CeO_2 slurries and SiO_2/Si_3N_4 surfaces. What's more, an atomic force microscope (Dimension ICON of Bruker) was utilized to map surface conditions of polished SiO_2 and Si_3N_4 wafers, where the obtained AFM images were scanned at a rate of 1 Hz on a surface area of $5 \times 5 \mu m$ for all wafers.

Table 1 Symbols and abbreviations of proper noun

Full name	abbreviation
Chemical mechanical polishing	CMP
Shallow trench isolation	STI
Ceria	CeO_2
Silicon dioxide	SiO_2
Silicon nitride	Si_3N_4
Material removal rate	MRR
Atomic force microscope	AFM
Scanning electron microscope	SEM
Deionized water	DIW
Thermogravimetric analysis	TGA
Polyethylpyrrolidone	PVP-K30
Polyethylene glycol	PEG
Polyacrylamide	PAM
Polyvinyl alcohol	PVA-124
Polypropylene glycol	PPG
Frequency	Δf
Dissipation	ΔD
The adsorption mass change	Δm

Fig. 2 Comparison test of CeO_2 bonded abrasive with different non-ionic surfactants after ball milling and subsiding for 0 and 7 days
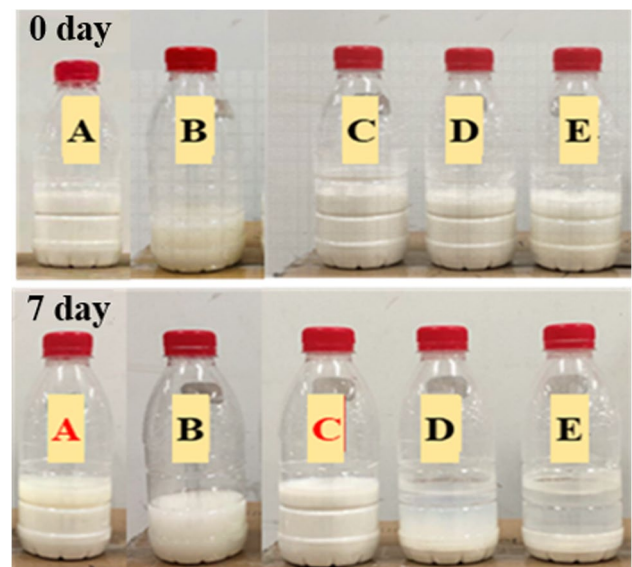
3 Results and discussion

3.1 Preparation and selection of CeO_2 slurries with various non-ionic surfactants

To modify and improve the polishing slurries for STI CMP process, various polymers as non-ionic surfactants which have different functional groups were introduced in the preparation process of CeO_2 slurries, involving polyethylene glycol (PEG, sample A), polyacrylamide (PAM, sample B), polyethylpyrrolidone (PVP-K30, sample C), polyvinyl alcohol (PVA-124, sample D), and polypropylene glycol (PPG, sample E). We give the symbols and abbreviations of all proper noun in Table 1. The settling results of CeO_2 bonded abrasives mixed with these non-ionic surfactants after 0 and 7 days of standing are shown in Fig. 2. It should

be emphasized that the presence of additional sediments and clear stratification results in poor dispersibility and stability for polishing slurries. It is apparent that the stability of CeO_2 slurries was excellent following the addition of surfactants C and A, which are PVP-K30 and PEG, respectively, while all of the CeO_2 slurries mixed with the other three surfactants displayed noticeable sedimentation.

The dispersion effects of PVP-K30 and PEG on CeO_2 particles were further compared, where the two mixed suspensions and the control group without any additive were naturally dried at room temperature to observe the particle morphology. As shown in Fig. 3a, after the addition of PVP-K30, it can be observed that the diameter of a single CeO_2 abrasive particle was approximately 60 nm. Meanwhile, there was a significant separation between each individual abrasive particle, indicating an excellent dispersion of CeO_2 slurries. Figure 3b presents the effect of PEG on CeO_2 particles, where the diameter of each single abrasive particle

was around 60 ~ 150 nm. Although a portion of CeO_2 particles was aggregated owing to the capillary force, the dispersion of the CeO_2 slurries was still improved. In contrast, the CeO_2 suspensions without any addition of surfactants were mapped in Fig. 3c. The diameter of CeO_2 particles was about 120 ~ 150 nm with a phenomenon of agglomeration. As shown, the addition of PVP-K30 and PEG is capable of enhancing the dispersion of CeO_2 abrasive particles.

The distinct dispersion effect of PVP-K30 and PEG on CeO_2 can be attributed to their structural differences. The functional group of $C=O$ in PVP monomer could form hydrogen bonds with CeO_2 and finally form the CeO_2-PVP-CeO_2 structure, which could produce a good dispersion effect on CeO_2, as shown in Fig. 4a. This structure was proposed in the CeO_2-SiO_2 composite particles synthesized by Lu et al. [13] to disperse and connect CeO_2 and SiO_2 particles uniformly. Moreover, the oxygen atoms of the C-O bond in PEG and the oxygen atoms in
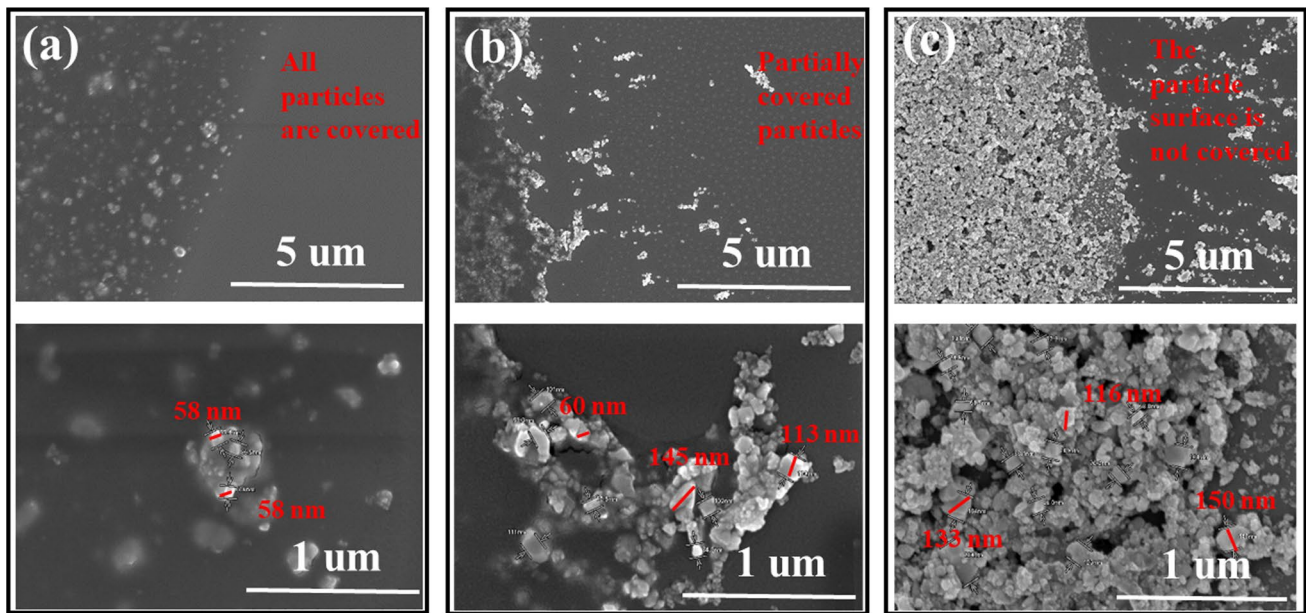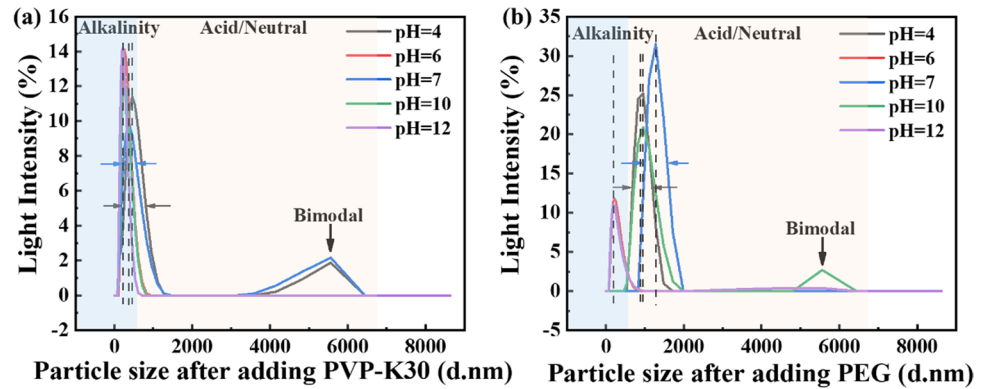

Fig. 3 SEM morphology of CeO_2 abrasive particles **a** with PVP-K30 added, **b** with PEG added, and **c** without any surfactant added after natural air drying

Fig. 4 Dispersion mechanism diagram of **a** PVP-K30 and **b** PEG with CeO_2

CeO$_2$ can be connected by hydrogen bonds, resulting in a CeO$_2$-PEG-CeO$_2$ structure, which could provide a good dispersion effect too (Fig. 4b). In particular, the oxygen atoms in PEG are separated by C-O and C–C bonds, while oxygen atoms in PVP are only separated by C–C bonds. The more C-O bonds of PEG than PVP-K30 make the folding effect of PEG more significant than that of PVP-K30 when forming hydrogen bonds with oxygen atoms of the same distance on CeO$_2$ particle surfaces, which makes the dispersion effect of PEG less than that of PVP-K30.

3.2 Stability of CeO$_2$ slurries with PVP-K30/PEG at different pH values

To further figure out the stability of CeO$_2$ slurries with PVP-K30 and PEG, particle size distribution of CeO$_2$ particles was compared at different pH values, as illustrated in Fig. 5. Quite similar tendency emerged with the addition of these two non-ionic surfactants that the half-peak width of CeO$_2$ particle size distribution in acidic and neutral environments is significantly larger than that in alkaline condition, indicating a more stable and uniform particle condition in high pH levels. Meanwhile, an interesting bimodal phenomenon both appeared under the action of PVP-K30 and PEG, where the pH levels for their occurrence are quite different.

Figure 6 depicts the specific particle sizes of CeO$_2$ abrasive at different pH values after the addition of PVP-K30 and PEG. The findings demonstrate that these two surfactants have a downward impact on CeO$_2$ abrasive particle sizes. Specifically, at pH values of 4, 6, 7, 10, and 12, the Z-average particle sizes of CeO$_2$ abrasive particle with PVP-K30 had a reduction of 77, 69, 84, 74, and 20%, while that with PEG decreased by 45, 75, 19, and 24%, respectively.

3.3 Effect of CeO$_2$ slurries with PVP-K30 and PEG on CMP process

The MRRs of Si$_3$N$_4$ in CeO$_2$-based slurries with the addition of PVP-K30 and PEG at different pH levels are depicted
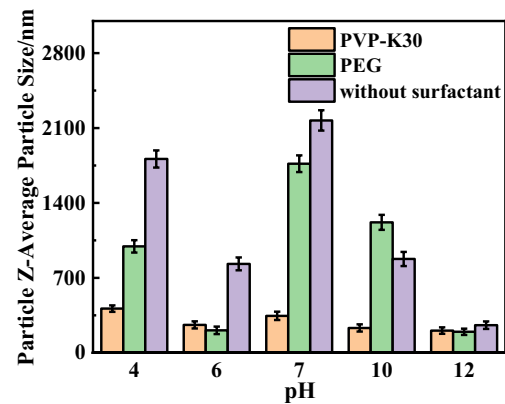
Fig. 6 Average particle sizes of CeO$_2$ with/without the addition of PVP-K30 and PEG at different pH values
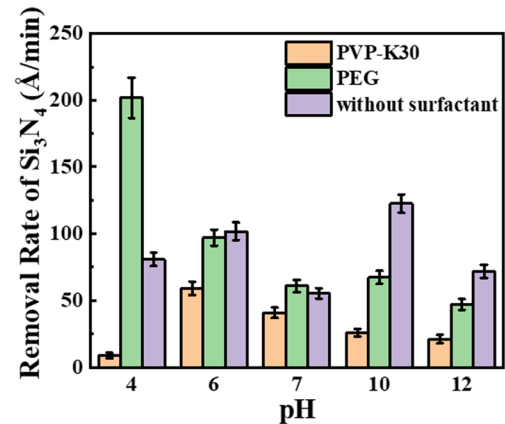
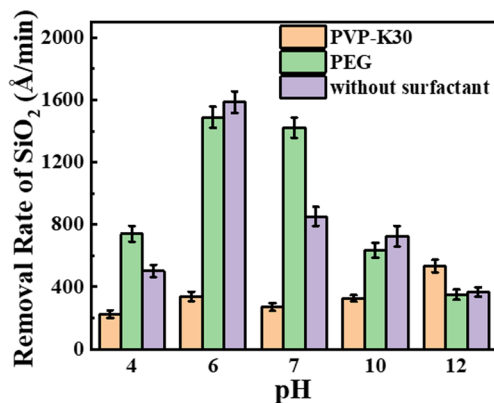**Fig. 7** MRRs of Si$_3$N$_4$ polished by CeO$_2$ slurries with/without the addition of PVP-K30 and PEG at different pH values

in Fig. 7. At pH values of 4, 6, 7, 10, and 12, the MRRs of Si$_3$N$_4$ polished by CeO$_2$ slurries with PVP-K30 were 9, 59, 41, 26, and 21 Å/min, respectively, achieving the goal for Si$_3$N$_4$ MRR of less than 50 Å/min. Compared with polished without any surfactant, the maximum Si$_3$N$_4$ MRR inhibition

of 89% could be achieved by the addition of PVP-K30 at pH 4. On the other hand, the MRRs of Si_3N_4 after polished by PEG in CeO_2 slurries were 202, 97, 61, 67, and 47 Å/min at different five pH values, respectively. It can be observed that at pH values of 4 and 7, PEG presents no inhibition impact on Si_3N_4 removal rates, whereas the MRRs of Si_3N_4 with PEG had a reduction of 5, 45, and 35% at pH values of 6, 10, and 12. By comparison, it was found that the inhibition of PVP-K30 on Si_3N_4 removal is stronger than that by PEG at all pH conditions.

Figure 8 presents the effect of PVP-K30 and PEG on SiO_2 MRRs in CeO_2-based slurries. When pH values were 4, 6, 7, and 10, the MRRs of SiO_2 polished by CeO_2 slurries with PVP-K30 were 226, 339, 271, and 327 Å/min, respectively. Compared with the polishing results without any surfactant, SiO_2 MRRs were inhibited by PVP-K30 with a reduction of 55, 79, 68, and 55%. However, the SiO_2 MRR (534 Å/min) with the addition of PVP-K30 was higher than that without any surfactant (368 Å/min) at pH 12. On the other hand, at five different pH conditions, the removal rates of SiO_2 after polished by CeO_2 slurries with PEG were 741, 1489, 1422, 635, and 350 Å/min, fluctuating considerably. At pH values of 6, 10, and 12, PEG inhibited SiO_2 MRRs slightly, which decreased by 6, 12, and 5%, respectively. As a result, it can be concluded that PVP-K30 could present a stronger inhibition on SiO_2 MRRs than PEG at pH values of 4, 6, 7, and 10.

Figure 9 shows the removal selectivity between SiO_2 and Si_3N_4 at different pH values polished using CeO_2 slurries with PVP-K30 and PEG added. At pH 4, 10, and 12, the removal selection ratios (~26, ~13, and ~25) between SiO_2 and Si_3N_4 polished by CeO_2 slurries with PVP-K30 were higher than those polished by slurries with PEG or without any surfactant addition, while with the addition of PEG, greater removal selection ratio could be achieved at pH 7. This demonstrates that PVP-K30 could play a role on removal selectivity at acidic and alkaline regions, whereas
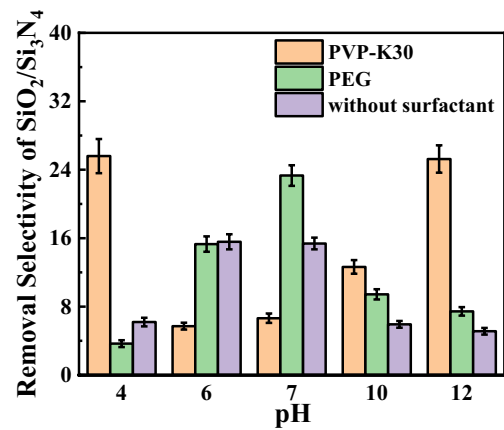
Fig. 9 Removal selectivity between SiO_2 and Si_3N_4 after polished by CeO_2 slurries with/without the addition of PVP-K30 and PEG at different pH values

PEG has the remarkable effect when the pH environment is neutral.

Figure 10 displays the surface roughness of SiO_2 and Si_3N_4 after polished by CeO_2 slurries with the addition of PVP-K30 or PEG at different pH levels. Although it seems that two non-ionic surfactants has little improvement on polished surface qualities, both of them meet the high demands (Ra < 1 nm), where the surface roughness of SiO_2 polished by CeO_2 slurries with PVP-K30 or PEG added was maintained at 0.20~0.32 nm, and that of Si_3N_4 was around 0.08~0.16 nm, respectively.

By characterizing the quantity and maximum depth of surface scratches, defects of polished SiO_2 and Si_3N_4 were identified. As presented in Fig. 11, the number of scratches in the range of 5×5 μm^2 on the SiO_2 and Si_3N_4 surfaces polished by CeO_2 slurries with added PVP-K30 and PEG was counted at various pH values. It was found that the number of scratches on polished SiO_2 surfaces decreased after the addition of PVP-K30 and PEG compared to that without any addition of surfactants, along with a same outcome of polished Si_3N_4 surfaces. Furthermore, the number of scratches on SiO_2 and Si_3N_4 surfaces is less in an alkaline environment than that in an acidic region.

Figures 12 and 13 show AFM images of SiO_2 wafers polished by CeO_2 slurries with PVP-K30 and PEG added under acidic, neutral, and alkaline environments, that is, pH values of 4, 7, and 10. The scratch depth of SiO_2 wafers polished by CeO_2 slurries with PVP-K30 in order from large to small is as follows: alkaline (~700 pm) > acidic (~500 pm) > neutral (~450 pm). However, quite different results were obtained when PEG was added in CeO_2 slurries, where the maximum scratch depth of ~700 pm occurred in neutral environment, whereas the slightest scratch depth was ~400 pm in acidic region. Similarly, Figs. 14 and 15 show the surface morphology of polished Si_3N_4 with the mixed slurries at pH

Fig. 8 MRRs of SiO_2 polished by CeO_2 slurries with/without the addition of PVP-K30 and PEG at different pH values

Fig. 10 Surface roughness of **a** SiO$_2$ and **b** Si$_3$N$_4$ after polished by CeO$_2$ slurries with/without the addition of PVP-K30 and PEG at different pH values
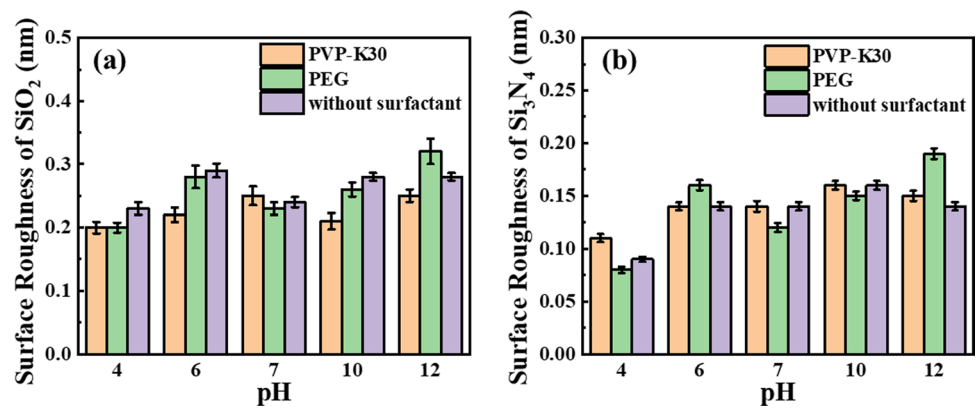
Fig. 11 Number of surface scratches on **a** SiO$_2$ and **b** Si$_3$N$_4$ after polished by CeO$_2$ slurries with/without PVP-K30 and PEG at different pH values
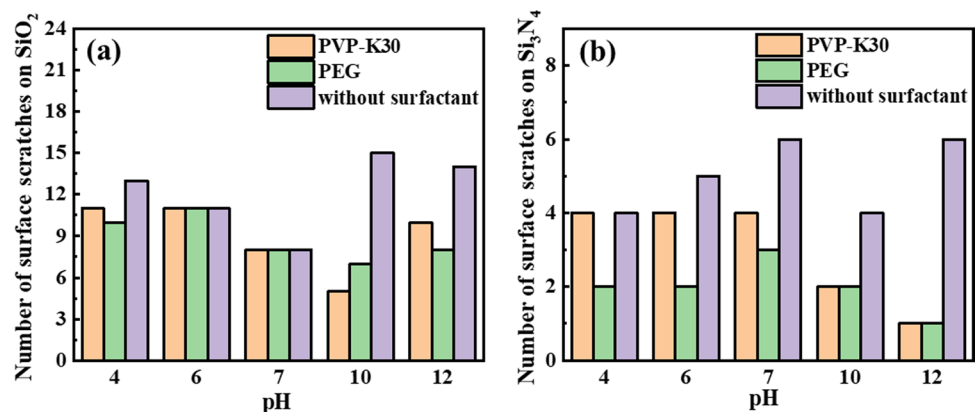
values of 4, 7, and 10. After polished by PVP-K30, the largest scratch depth on Si$_3$N$_4$ surfaces occurred in acidic condition of ~ 450 pm, followed by neutral and basic environment of ~ 400 pm. After polished by PEG, the maximum scratch depth of Si$_3$N$_4$ surfaces can be found in alkaline condition (~ 450 pm), followed by neutral (~ 350 pm), and then acid environment (~ 300 pm). In general, the maximum scratch depth of polished SiO$_2$ surfaces was greater than that of Si$_3$N$_4$ surfaces at the same pH condition. Owing to the presence of mechanical action during material removal, SiO$_2$ has a higher removal rate than Si$_3$N$_4$, accompanied by greater surface wear than Si$_3$N$_4$, and thus a greater maximum surface scratch depth for SiO$_2$.

3.4 Adsorption behavior of PVP-K30 and PEG on SiO$_2$ and Si$_3$N$_4$ surfaces

There is a uniform rule at pH values of 4, 6, 7, and 10 that PVP-K30 has a greater inhibitory effect on the removal of SiO$_2$ and Si$_3$N$_4$ than PEG. The two mixed suspensions were selected at pH value of 4 to analyze their adsorption on the surfaces of SiO$_2$ and Si$_3$N$_4$. A quartz crystal microbalance was used as a characterization instrument, DIW was injected into SiO$_2$ (or Si$_3$N$_4$) as the base solution, and baseline frequency signals were measured after stabilization. When CeO$_2$

slurries containing PVP-K30 or PEG were injected into SiO$_2$ (or Si$_3$N$_4$) chips at a flow rate of 0.2 mL/min, the vibration frequency of SiO$_2$ (or Si$_3$N$_4$) changed. Simultaneously, the frequency reduction of the third overtone and the dissipation caused by adsorption at 25 ℃ were recorded. When the adsorption amount gradually increased to a stable value, the vibration frequency and surface dissipation of SiO$_2$ (or Si$_3$N$_4$) tended to stabilize. The vibration frequency of the stabilized SiO$_2$ (or Si$_3$N$_4$) after passing through CeO$_2$ slurries containing PVP-K30 or PEG solution was compared with the vibration frequency of SiO$_2$ (or Si$_3$N$_4$) when passing through DIW, and the difference was taken as the resonance frequency (Δf) of the adsorption of PVP-K30 and PEG molecules on SiO$_2$ and Si$_3$N$_4$. Similarly, the change in the surface dissipation (ΔD) of SiO$_2$ and Si$_3$N$_4$ was calculated.

When the dissipation is sufficiently small (ΔD < 10|Δf|), the adsorption film is rigid and has low viscoelasticity. According to Eq. (1), the frequency change can be converted into the adsorption mass change (Δm) using the Sauerbrey equation [14]:

$$\Delta m = -C\frac{\Delta f}{n} \tag{1}$$

where C is a constant (17.7 ng·Hz^{-1}·cm^{-2}) related to the properties of the quartz crystal and n is the overtone

Fig. 12 Surface morphology of SiO_2 polished by CeO_2 slurries with PVP-K30 added at **a** pH 4, **b** pH 7, and **c** pH 10
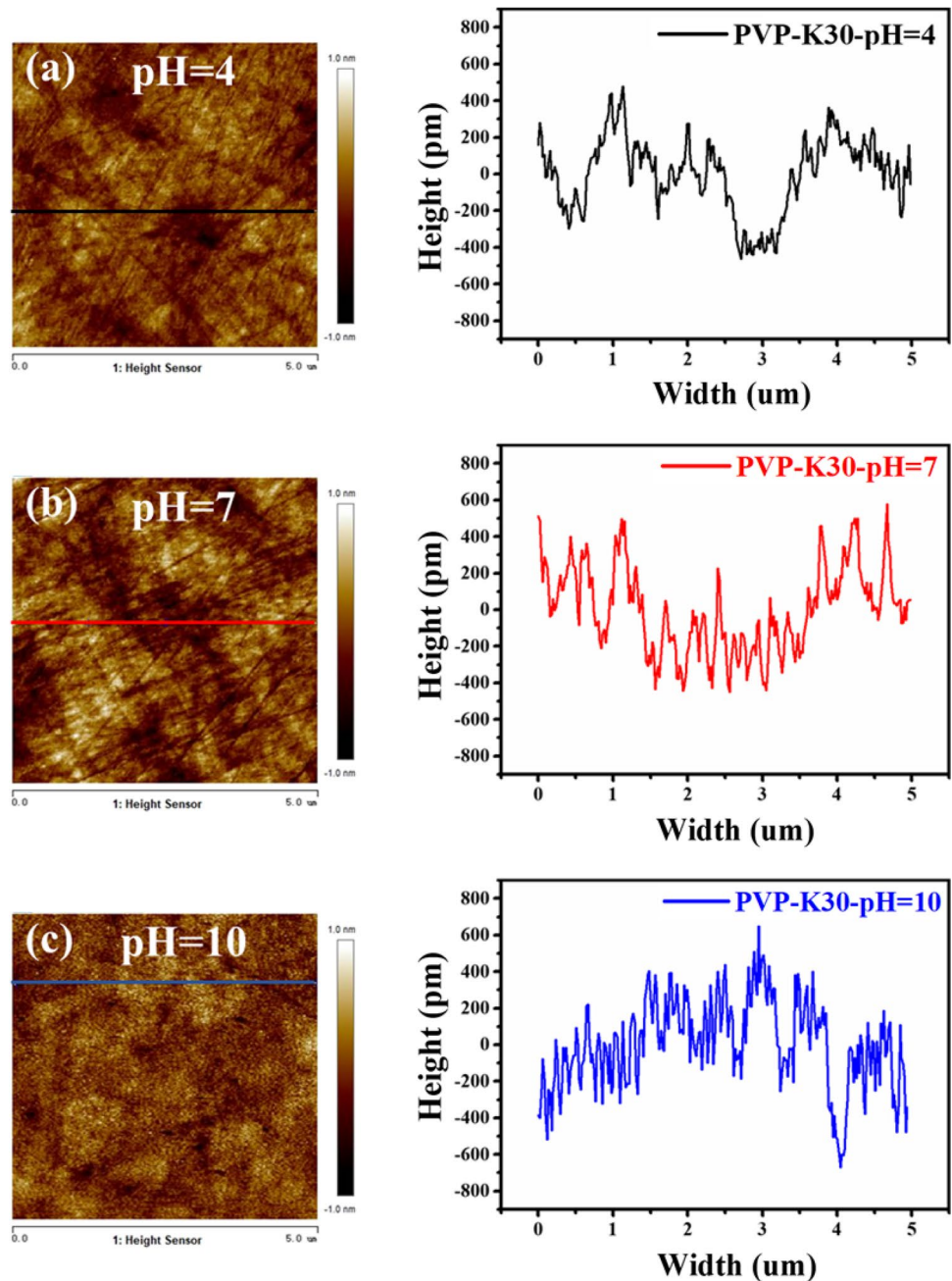
of oscillation (3 for SiO_2 and Si_3N_4 wafers with 150 mm diameter).

As shown in Fig. 16, when the adsorption amount of PVP-K30 on the SiO_2 surface gradually became stable, the resonance frequency of PVP-K30 molecular adsorption on SiO_2 was approximately 23 Hz, and the change in surface dissipation was approximately 3 ppm. As shown in Fig. 17, when the adsorption amount of PEG on the SiO_2 surface gradually stabilized, the Δf of PEG molecule adsorption on SiO_2 was approximately 10 Hz with a ΔD approximately of 1.2 ppm. In both cases, the dissipations are sufficiently small ($\Delta D < 10|\Delta f|$), indicating that the adsorption films of

PVP-K30 and PEG on SiO_2 surfaces are rigid and have low viscoelasticity. The adsorption mass on the SiO_2 surface (Δm) can be calculated using Eq. (1) as 240 ng and 104 ng, respectively.

The adsorption behavior of PVP-K30 and PEG on Si_3N_4 wafers was identified using the same approach, as depicted in Figs. 18 and 19. The same conclusions can be drawn that the adsorption films of PVP-K30 and PEG on Si_3N_4 surfaces are rigid with low viscoelasticity and have an adsorption mass of around 198 and 73 ng, respectively. It was found that the adsorption mass of PVP-K30 on SiO_2 and Si_3N_4 surfaces was greater than that of PEG, which could explain

Fig. 13 Surface morphology of SiO$_2$ polished by CeO$_2$ slurries with PEG added at **a** pH 4, **b** pH 7, and **c** pH 10
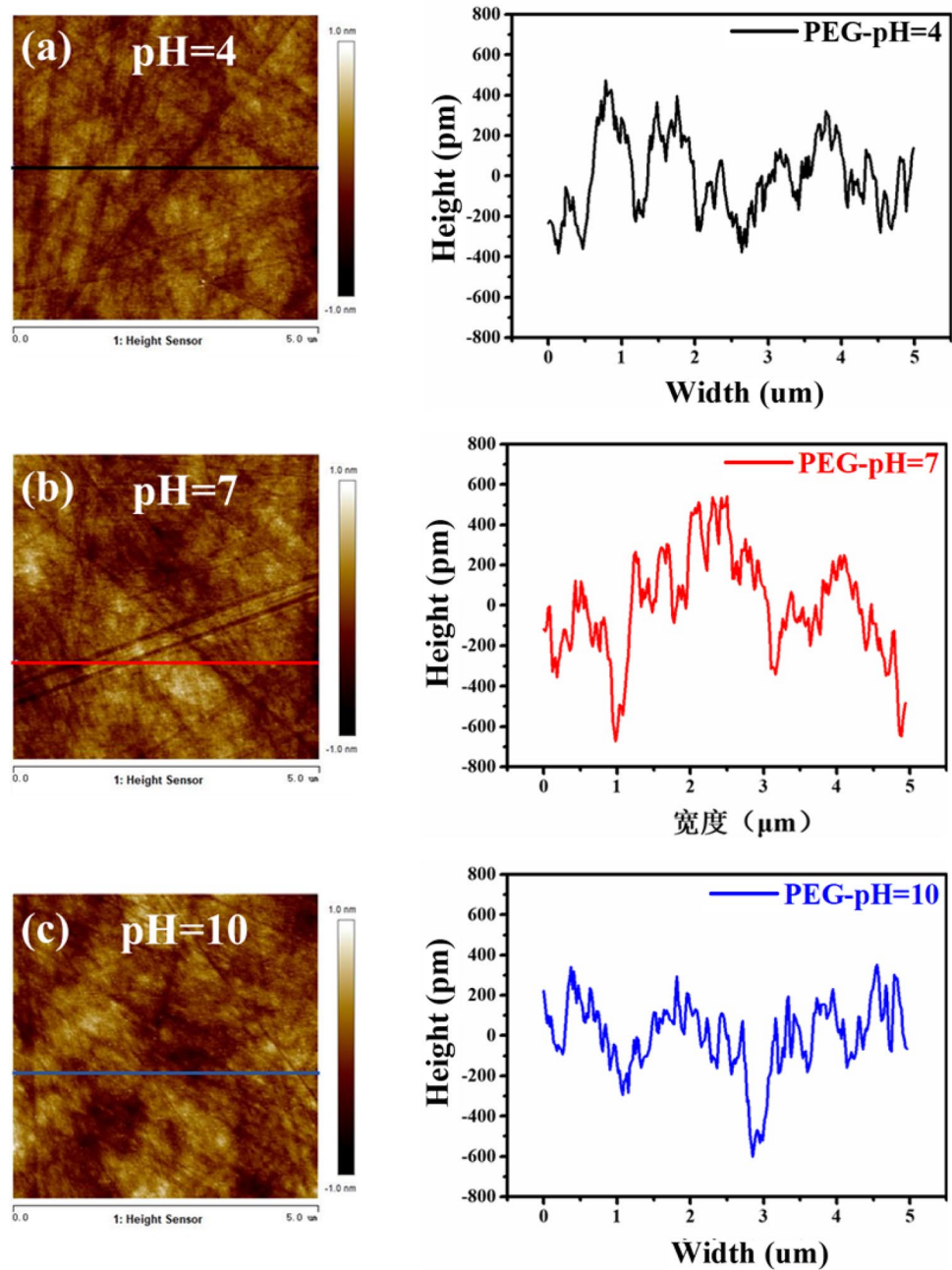
why when the pH value was 4, PVP-K30 had a stronger inhibitory effect on the removal of SiO$_2$ and Si$_3$N$_4$ than that of PEG.

3.5 Adsorption behavior of PVP-K30 and PEG on CeO$_2$ particles

When the pH values are 4, 6, 7, and 10, PVP-K30 has a greater inhibition on the removal of SiO$_2$ and Si$_3$N$_4$ than that of PEG. At a pH value of 6, the two mixed slurries were subjected to thermogravimetric analysis. It is known that the boiling point of PEG is greater than 250 ℃ and that of PVP-K30 is greater than 350 ℃. In Fig. 20, with an increasing temperature, the two mixed slurries lose weight gradually at first and then begin to lose weight rapidly when the temperature is close to 100 ℃. This stage is a part of the water evaporation process. The weight loss beyond 100 ℃ is the decomposition stage of the remaining solid substances at high temperatures. The mass of the mixture of PEG and CeO$_2$ remained unchanged from 100 to 250 ℃ after the first stage of rapid weight loss (0 to 100 ℃). It underwent weight loss in the second stage at 250 ℃, and its mass did not change beyond approximately 380 ℃. The mixture of PVP-K30 and CeO$_2$ experienced rapid weight loss in the

Fig. 14 Surface morphology of Si$_3$N$_4$ polished by CeO$_2$ slurries with PVP-K30 added at **a** pH 4, **b** pH 7, and **c** pH 10
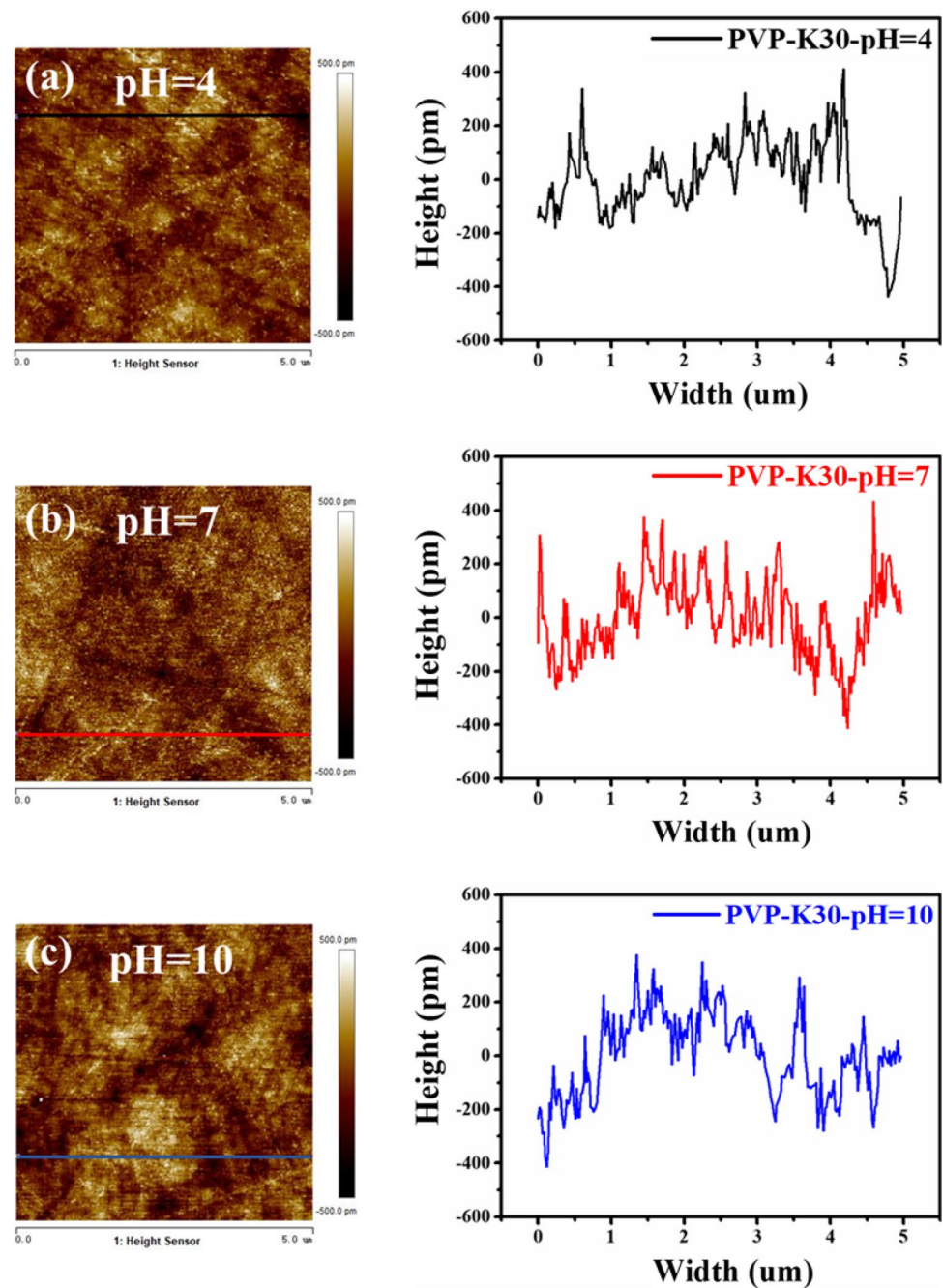

first stage (0–100 ℃) and its mass remained unchanged at approximately 100–350 ℃. It experienced weight loss at 350 ℃ from the second stage, and its mass did not change beyond approximately 500 ℃. After adding PEG and PVP-K30, the weight loss temperature in the second stage was consistent with the boiling points of PEG and PVP-K30. This indicates that PEG and PVP-K30 are still adsorbed on the abrasive surface during water evaporation. When DIW is completely evaporated, it needs to be heated to the boiling point of PEG and PVP-K30 before they leave the abrasive surface.

3.6 Zeta potential analysis of SiO$_2$ and CeO$_2$ slurries with PVP-K30 and PEG

To further explore the removal mechanisms, zeta potentials of CeO$_2$ mixed slurries with PVP-K30 and PEG added were analyzed at different pH values, as shown in Fig. 21. After adding PEG and PVP-K30, the surface zeta potentials are positive at pH values of 4 and 6, indicating that there is a gravitational interaction between CeO$_2$ abrasive particles and SiO$_2$ surfaces. The absolute value of the zeta potential of PVP-K30 and CeO$_2$ mixed suspension is less than that of
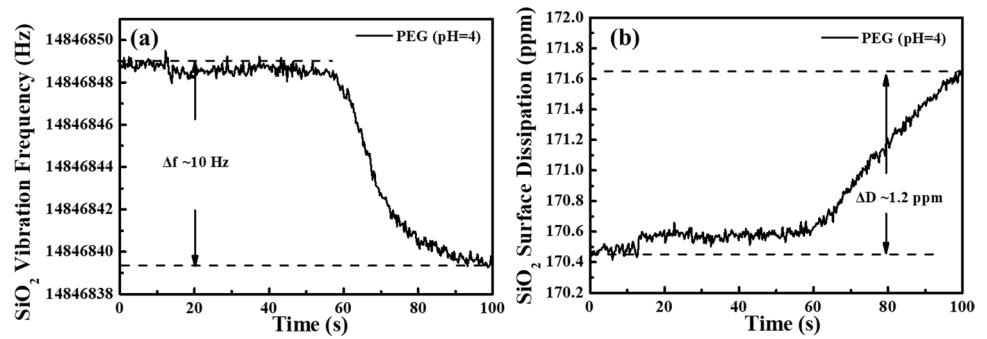
**Fig. 15** Surface morphology of Si$_3$N$_4$ polished by CeO$_2$ slurries with PEG added at **a** pH 4, **b** pH 7, and **c** pH 10
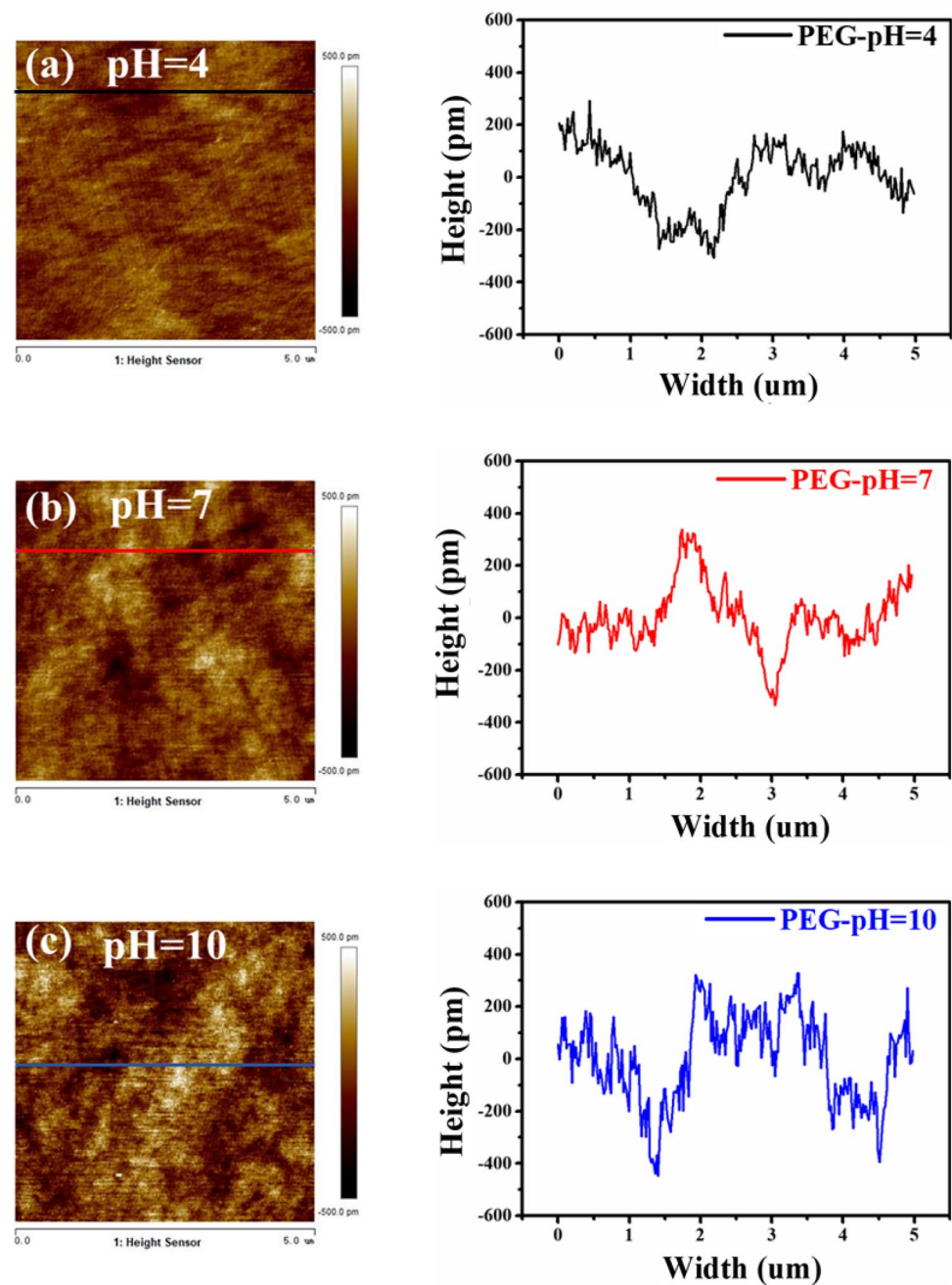
**Fig. 16** **a** Vibration frequency and **b** surface dissipation of PVP-K30 in CeO$_2$ slurries on SiO$_2$ surfaces at pH 4
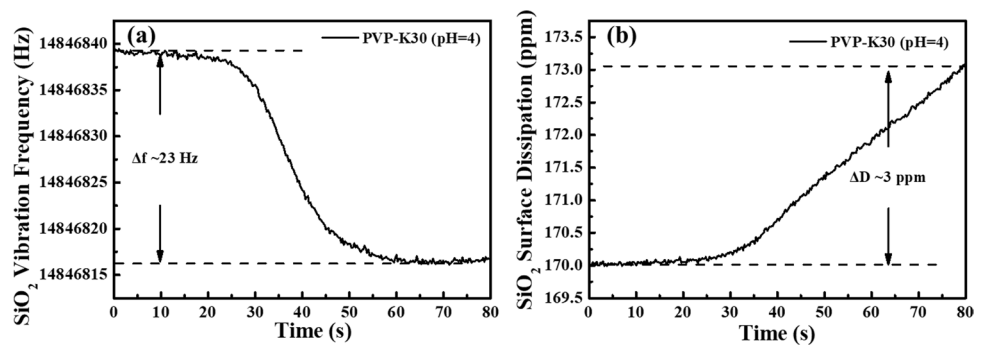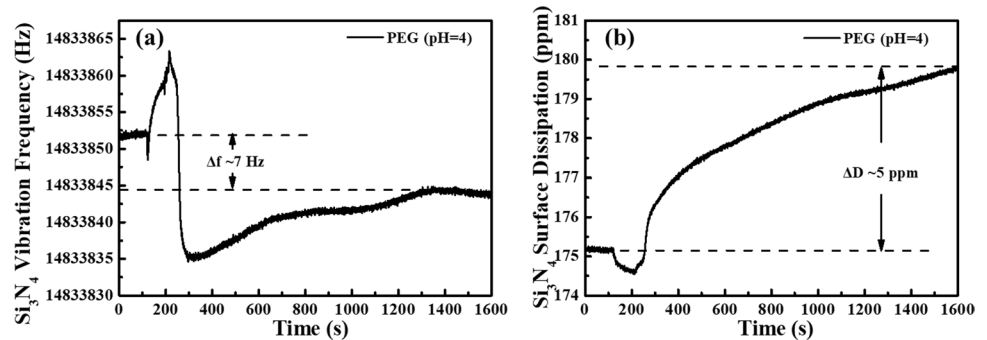
Fig. 17 **a** Vibration frequency and **b** surface dissipation of PEG in CeO$_2$ slurries on SiO$_2$ surfaces at pH 4

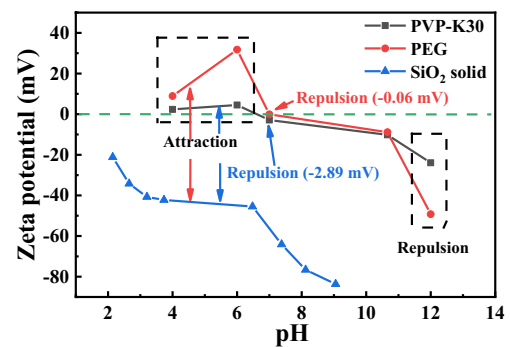**Fig. 18** **a** Vibration frequency and **b** surface dissipation of PVP-K30 in CeO$_2$ slurries on Si$_3$N$_4$ surfaces at pH 4
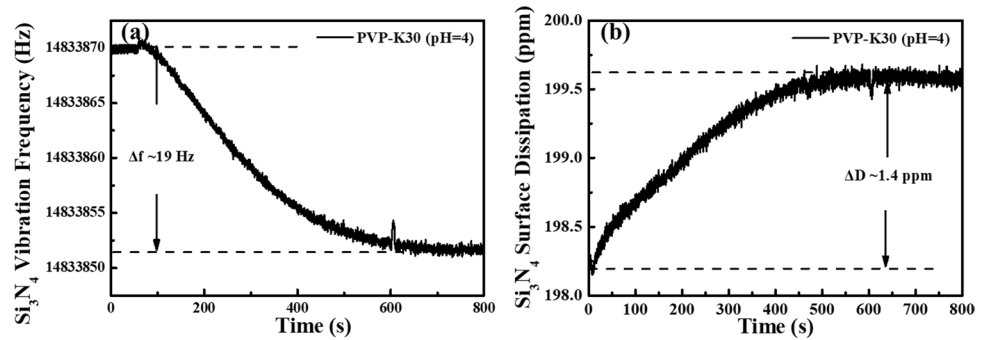
Fig. 19 **a** Vibration frequency and **b** surface dissipation of PEG in CeO$_2$ slurries on Si$_3$N$_4$ surfaces at pH 4
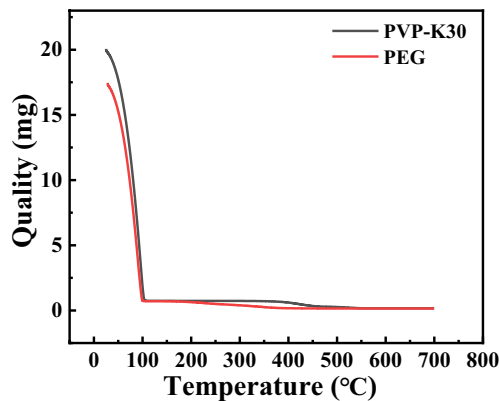
Fig. 20 TGA analysis curves of CeO$_2$ mixed slurries with PVP-K30 and PEG

Fig. 21 Zeta potentials of CeO$_2$ mixed slurries with **a** PVP-K30 and **b** PEG and **c** SiO$_2$ solid surface at different pH values

PEG and CeO_2 mixed one; this shows that the gravity of the former and SiO_2 is less than that of the latter. This further explains why PVP-K30 has stronger removal inhibition on SiO_2 than PEG at pH values of 4 and 6. The surface zeta potentials of the two mixed suspensions are negative at pH values of 7, 10, and 12, and there will be a repulsive force between CeO_2 abrasive particles and SiO_2 surfaces. When pH values are 7 and 10, the absolute value of zeta potentials of PVP-K30 and CeO_2 mixed suspension is greater than that of PEG and CeO_2 mixed one, which proves that the repulsion between the former and SiO_2 is greater than that of the latter. When the pH value is 12, the absolute value of zeta potential of the CeO_2 mixed slurry with PVP-K30 added is smaller than that of the CeO_2 mixed slurry with added PEG, which proves that the repulsion between the former and SiO_2 is smaller than that of the latter. This further explains why PVP-K30 has stronger removal inhibition on SiO_2 than PEG at pH values of 7 and 10. The removal rate of SiO_2 after adding PEG is lower than that after adding PVP-K30 when the pH value is 12.

Here, the dispersion effects of various non-ionic surfactants on CeO_2 particles were compared. It was found that PVP-K30 and PEG can uniformly disperse CeO_2 particles and achieve suitable removal selectivity between SiO_2 and Si_3N_4. We focused on the effect of CeO_2 polishing slurry containing non-ionic surfactants on the surface quality of polished SiO_2 and Si_3N_4 wafers. In addition, the effect of pH value on the selectivity of SiO_2 and Si_3N_4 removal provides a reference for subsequent research on polishing slurry systems.

4 Conclusions

In this study, the influence mechanism of the non-ionic surfactants PVP-K30 and PEG on the dispersion of CeO_2 slurries and the removal of SiO_2 and Si_3N_4 were investigated. The following conclusions were drawn from the study:

(1) Non-ionic surfactants can be adsorbed on CeO_2 abrasive particles by forming hydrogen bonds, where the adsorption mode is slightly affected by pH values. The Z-average particle sizes of CeO_2 suspensions were 200 ~ 400 nm at different pH values after the addition of PVP-K30.

(2) Among various non-ionic surfactants, PVP-K30 has a stronger dispersion effect on CeO_2 particles than PEG since PEG has more C-O bonds than PVP-K30, which makes the folding effect of chain polymer PEG more significant than that of PVP-K30 when forming hydrogen bonds with oxygen atoms at the same distance on the CeO_2 surface.

(3) At pH values of 4, 6, 7, and 10, PVP-K30 showed stronger inhibition on SiO_2 and Si_3N_4 than PEG did. This is because the zeta potentials of the mixed suspension of PVP-K30 and CeO_2 is smaller than that of the PEG mixed

one, which makes the suspension and SiO_2 more repulsive. Moreover, PVP-K30 has a greater adsorption capacity on SiO_2 and Si_3N_4 surfaces than that of PEG, reducing the contact between CeO_2 abrasive particles and SiO_2/Si_3N_4 surfaces. At a pH value of 4, PVP-K30 showed the strongest inhibition on Si_3N_4 removal, and the removal rate decreased from 81 to 9 Å/min.

As a result, it can be concluded that the performance of ceria slurries used in STI CMP process can be improved by the addition of non-ionic surfactant PVP-K30 at pH 4.

Declarations

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